REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 05 October 2015	**2. REPORT TYPE** Briefing Charts	**3. DATES COVERED** *(From - To)* 15 September 2015 - 05 October 2015

4. TITLE AND SUBTITLE Advanced Fuel Quality Assurance Standards Based On Thermal Testing & Chemometric Modeling	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) M. Billingsley, D. Pamplin, N. Keim, B. Hill-Lam, C. Wilhelm, R. Synovec	**5d. PROJECT NUMBER**
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER Q0A4
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRC 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680	**8. PERFORMING ORGANIZATION REPORT NO.**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB, CA 93524-7048	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) **AFRL-RQ-ED-VG-2015-367**

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
For presentation at 14th International Symposium on the Stability, Handling, & Use of Liquid Fuels; Charleston, SC; 05 Oct 2015
PA Case Number: #15588; Clearance Date: 9/24/2015

14. ABSTRACT
Briefing Charts/Viewgraphs

15. SUBJECT TERMS
N/A

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** M. Billingsley
a. REPORT **Unclassified**	**b. ABSTRACT** **Unclassified**	**c. THIS PAGE** **Unclassified**	SAR	26	**19b. TELEPHONE NO** *(include area code)* N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

ADVANCED FUEL QUALITY ASSURANCE STANDARDS BASED ON THERMAL TESTING & CHEMOMETRIC MODELING

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IASH 14th Int'l. Symposium
Charleston, SC
Oct 2015

Acknowledgments

- **Jose Maniwang, Lindsey Hicks**
  DLA Energy (DQT), Ft. Belvoir, VA

- Tim Edwards (AFRL/RQTF)
- Linda Shafer, Matt DeWitt, coworkers (UDRI)
- Steve Westbrook, George Wilson (SwRI)
- Joel Moreno, Indresh Mathur (Haltermann Solutions)

Outline

- Motivation/Background
- Approach
- Referee Fuel Set
- Thermal Integrity Test Method and Results
- Model Development and Results
- Future Work

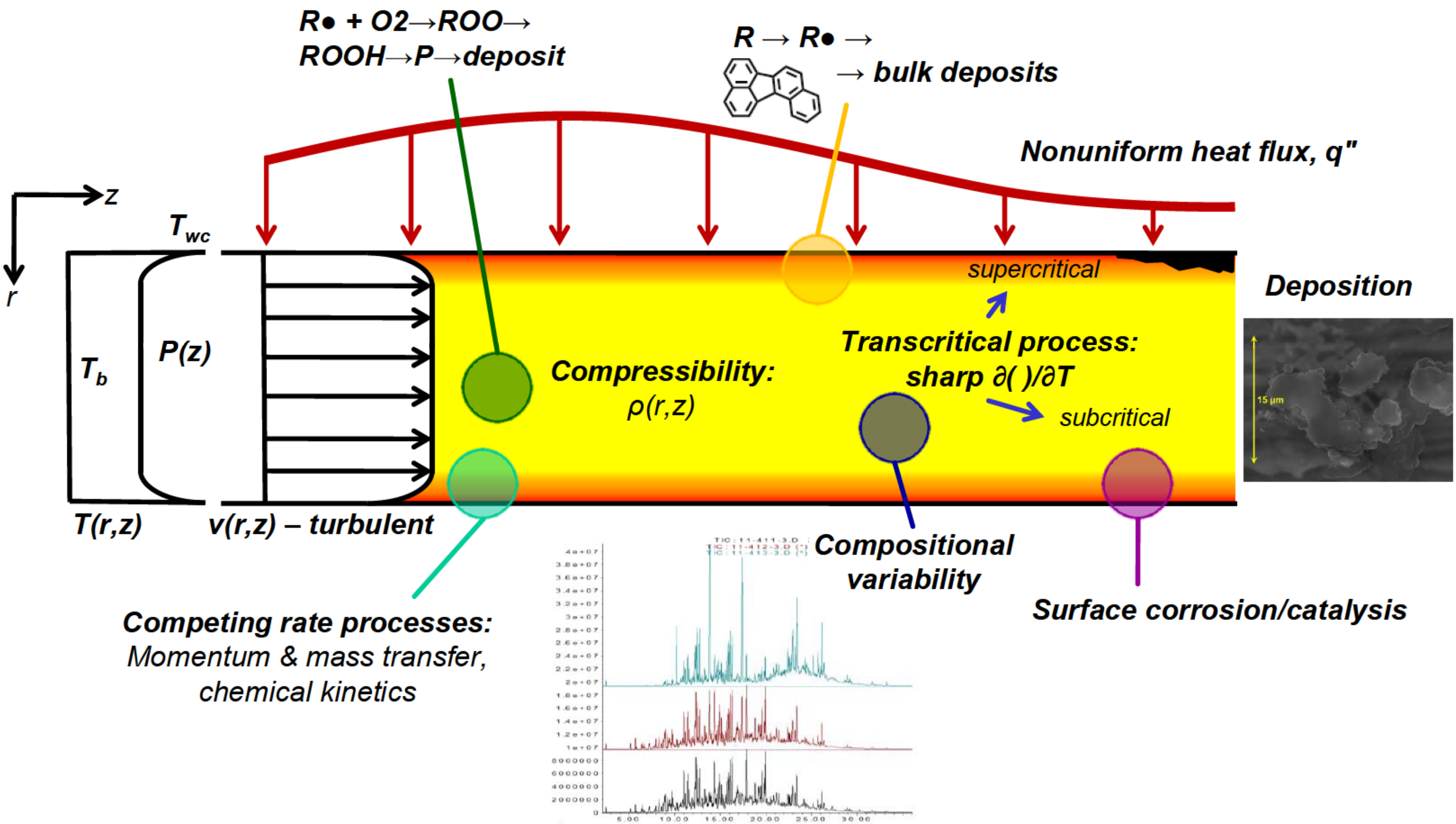
Motivation: Fuel Quality Assurance

- Propulsion fuel performance, quality, and suitability ***must be verified***
- This challenge is faced by:
  - Aerospace propulsion development/demonstration activities
  - Agencies who procure fuels for DoD use
  - Fuel manufacturers and suppliers
- Many requirements to consider:
  - Propellant cost
  - Support operations/infrastructure
  - Product availability & sustainability
  - **Functional performance**: combustion, cooling, lubrication…
    - ***Fuel thermal stability and material compatibility***

Aerospace Cooling System Conditions and Environments

Application	T_{wall} (°F)	$T_{fuel, bulk}$ (°F)	Pressure (psi)	Heat Flux (Btu/in²s)	Material
Rockets	500-900	100-500	700-7000	10-120	Cu alloys
Hypersonics	1200-1500	100-1300	500-1000	0.5-2	Ni alloys
Aircraft	300-400	100-300	500-800	<1	SS alloys

Liquid Rocket Engine (LOX/Kerosene) Regenerative Cooling Environment

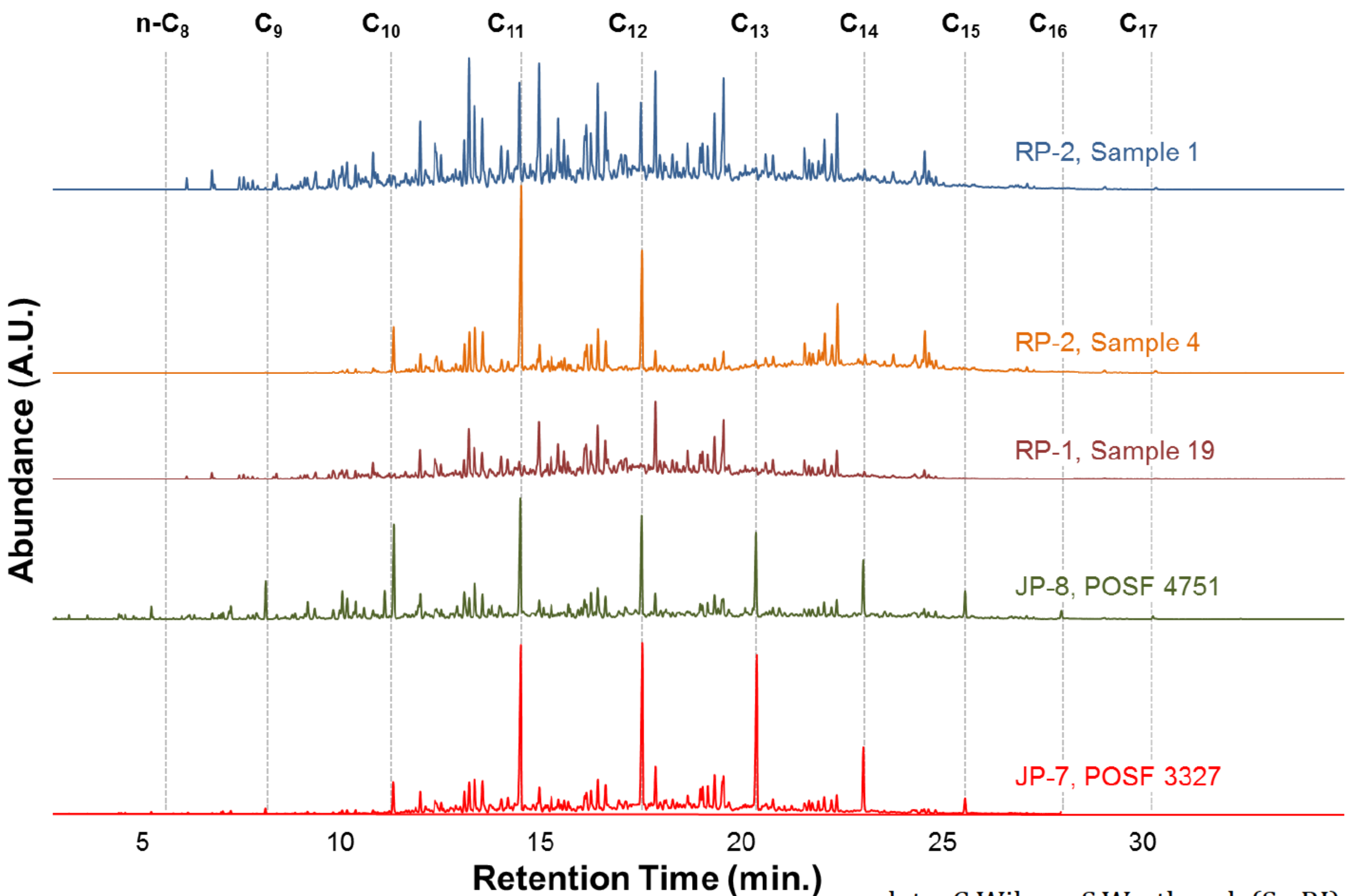


Background
1. Fuel Specification

	ASTM Method	JP-5	Jet A	RP-1	RP-2
Specification		MIL-DTL-5624U	ASTM D1655-15	MIL-DTL-25576E	MIL-DTL-25576E
Requirement, Units					
Distillation, °C					
IBP	D86	report		report	report
10% recovered		<205	<205	(185-210)	(185-210)
20% recovered		report			
50% recovered		report	report	report	report
90% recovered		report	report	report	report
End point		<300	<300	(<274)	(<274)
Density/15°C, kg/L	D1298	0.788-0.845	0.775-0.840	0.799-0.815	0.799-0.815
Viscosity/-20°C, mm^2/s	D445	<8.5	<8.0	<16.5[b]	<16.5[b]
Flash Point, °C	D93[c]	>60	>38	(>60)	(>60)
Freezing Point, °C	D2386[d]	<-46	<-40[e]	(<-51)	(<-51)
Net Heat of Combustion, MJ/kg	varies[f]	>42.6	>42.8	(>43.0)	(>43.0)
Hydrogen, mass %	varies[g]	>13.4	>13.4[h]	>13.8	>13.8
Aromatics, vol %	D1319	<25.0	<25.0	<5	<5
Olefins, vol %	D1319			<2.0	<1.0
Total sulfur, mass%	varies[i]	<0.3	<0.3	<0.003	<0.00001
Mercaptan sulfur, mass%	D3227	<0.002[j]	<0.003[j]	<0.0003	
Thermal Stability: ΔP change, mmHg	D3241[k]	<25	<25		report

- Specification review and development activities are important for fuel qualification
- Physical, chemical spec limits are influenced by operational factors:
  - Performance
  - Handling/storage
  - Cost/Availability
- Neither engine performance *nor* fuel chemical composition are specified *per se*…

Background
2. Compositional Variation



data: G.Wilson, S.Westbrook (SwRI)

Background
3. (Lack of) Thermal Performance Test

ASTM D3241 (JFTOT) Results
(Shaded fuels shown in previous slide)

325°C, 5 hr. ← → 355°C, 5 hr.

Fuel Type	JP-7	JP-8	RP-1	RP-2	RP-2	RP-TS-5	RP-2	Fuel Type	RP-1	RP-1
Designation	POSF 3327	POSF 4751	Sample 19	Sample 4	Sample 1	Sample 14	Sample 6	Designation	Sample 18	Sample X
Tube Deposit Rating Code	<2	>4AP[a]	<2	<2	<2	<2	<2	Max ΔTDR, spun	35-38 (17)[b]	5
Maximum ΔP, mmHg	0.1	280.1	0.1	0	0.1	0	0	Maximum ΔP, mmHg	0	0

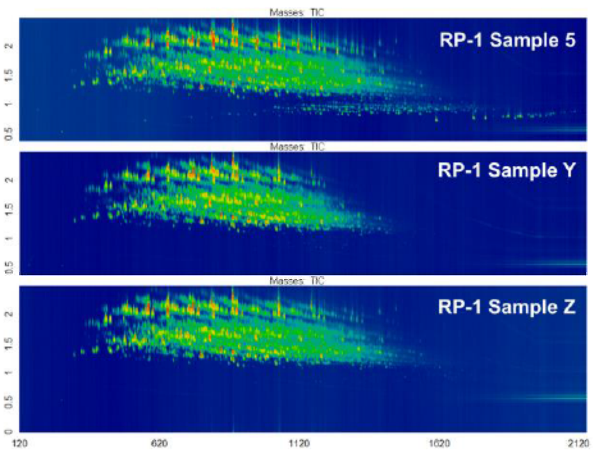
[a] "A" denotes abnormal deposit; "P" denotes peacock deposit.
[b] Filtered

data: G.Wilson, S.Westbrook (SwRI)
R.Cook (AFRL), M.Thiede (AFPET)

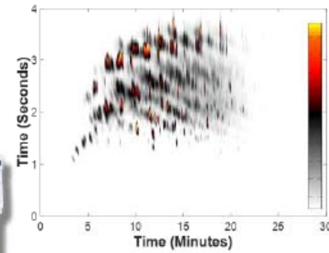
- Rocket kerosene is not quality tested for thermal stability or material compatibility prior to delivery
  - RP-1 is not tested. RP-2 ***is*** tested with ASTM D3241 (JFTOT) but results are "report only"
- JFTOT method ***may be*** valuable for screening very low performing fuels (contamination, alternative sources)…
- ***But the method is inadequate for ensuring fuel quality as increasingly demanding thermal environments arise***

AFQTMoDev Project Structure

Fuel Compositional Variation



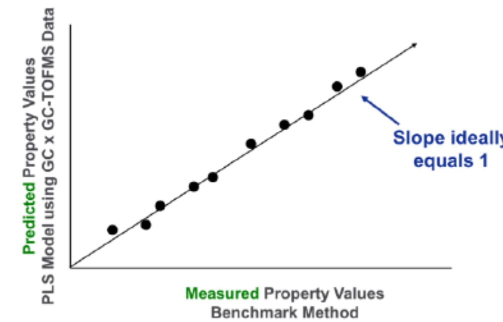
1. Optimize Composition
2. Specification Limits



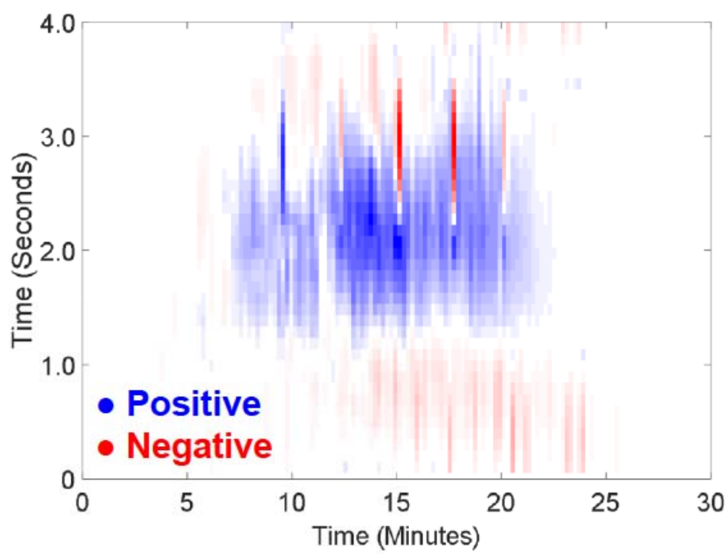
GCxGC-TOFMS
3D Chemical Data

LECO RC612
Test section analysis

CRAFTI
Thermal Integrity Index (TII)



PLS Model Development

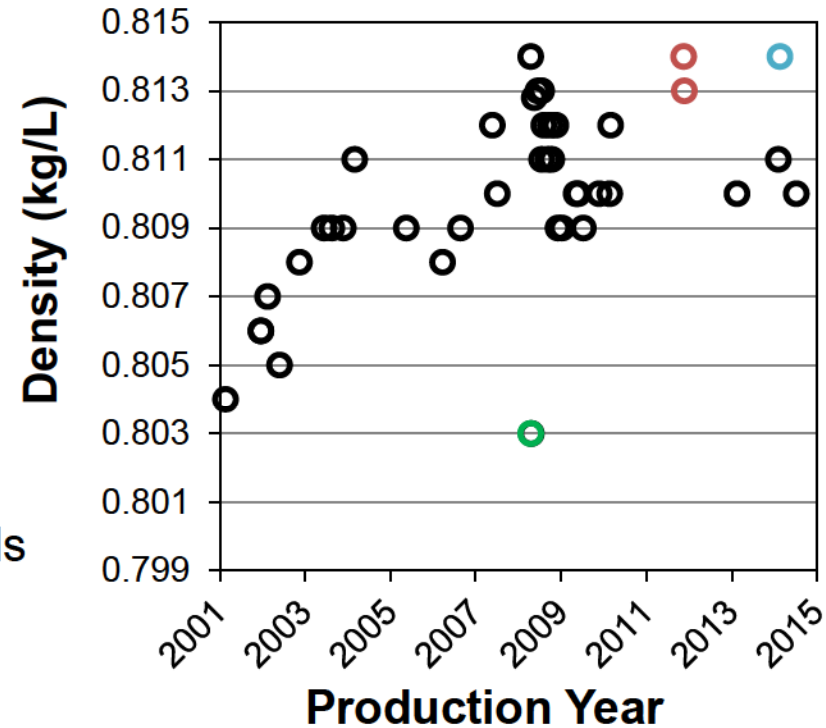


Compound Correlation to TII

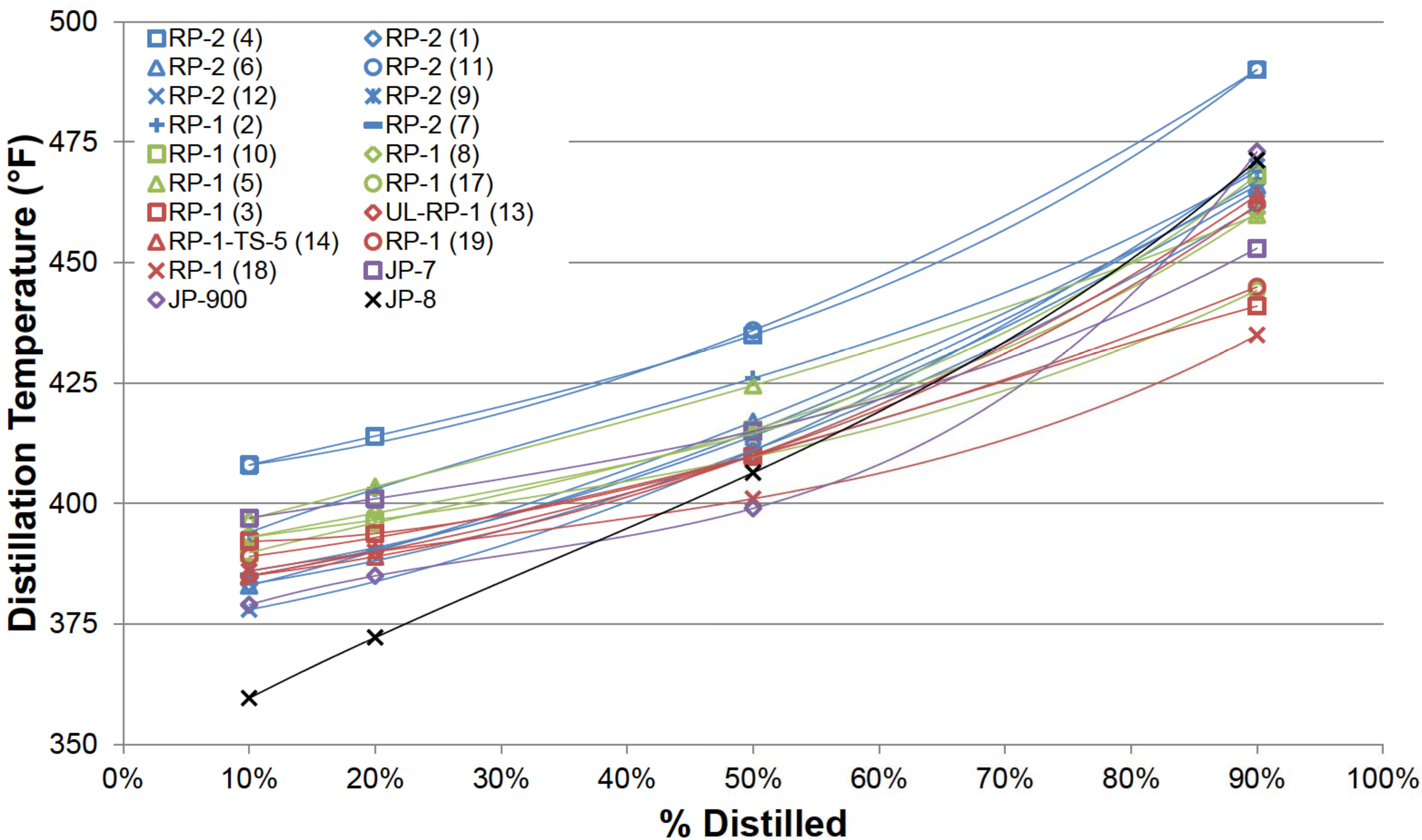
Referee Fuel Set

- Criteria for fuel selection
  - Multicomponent: distribution of hydrocarbon species and/or types
  - Possess heteroatom species diversity
  - Span the compositional range of fuels meeting MIL-DTL-25576E: not necessarily "today's fuel"
  - Meet aerospace fuel designations for health/flammability/reactivity, etc.

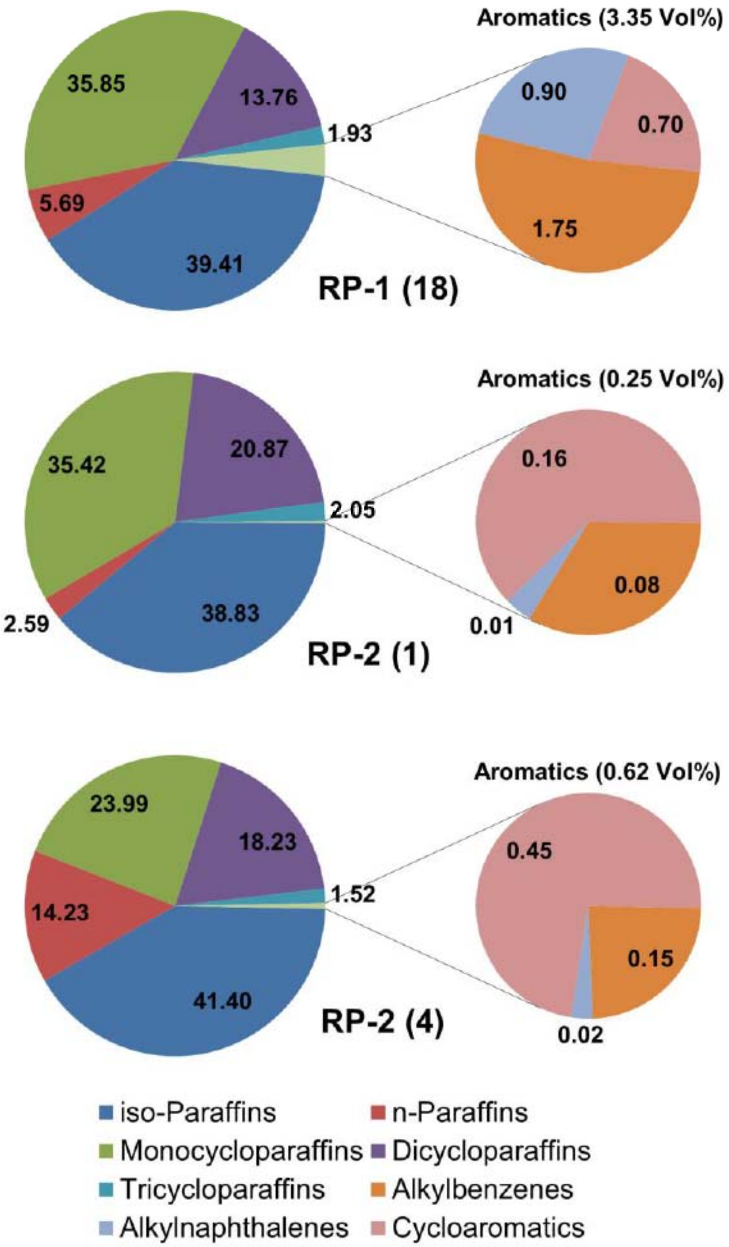
- What we ended up with
  - 51 compositionally unique fuels (or potential blend materials – single/multicomponent)…
  - 19 evaluated for thermal integrity and included in chemometrics/modeling
  - (8) RP-2,(9) RP-1, JP-7, JP-900
  - 3 available from previous SwRI project
  - Less than ideal compositional variation
    - Produced on demand – no repository of historical fuels
    - Relatively consistent production past 20 years
    - Several "interesting" fuels contained common feedstocks

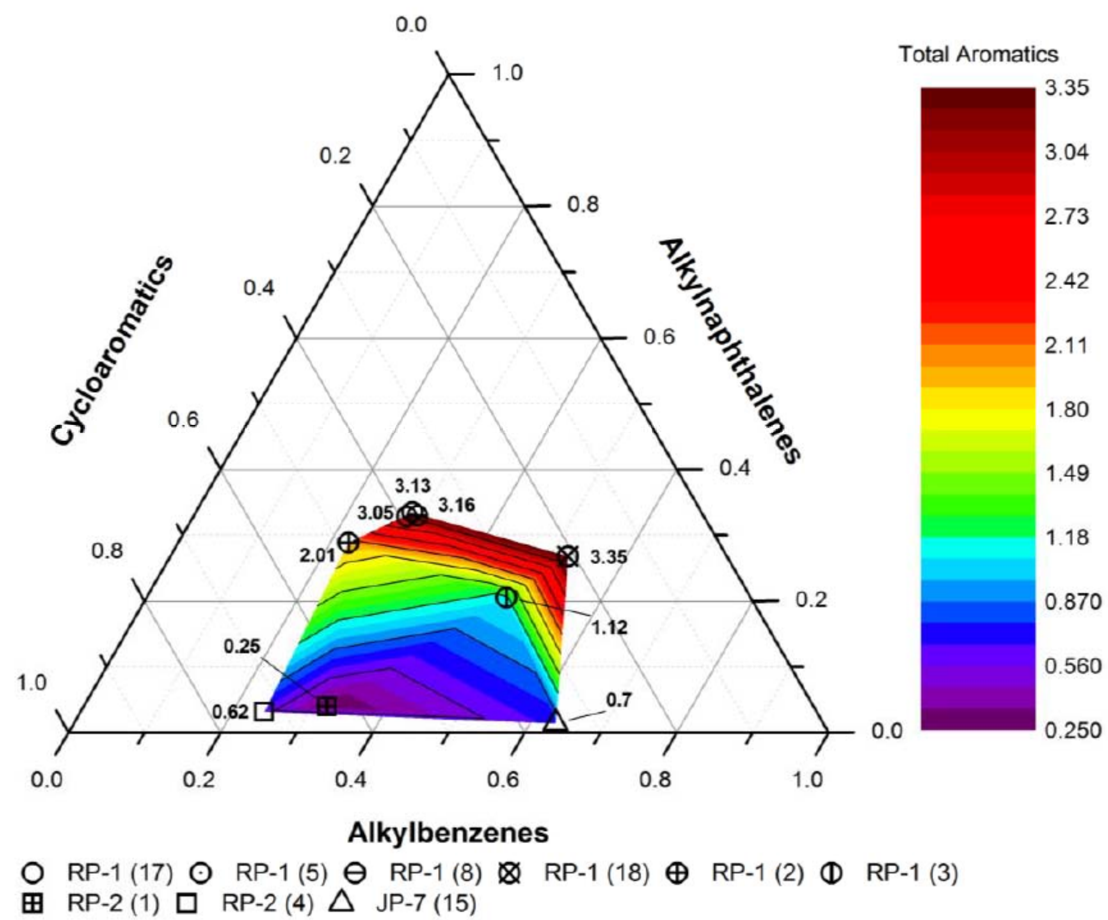


Referee Fuel Set Variation

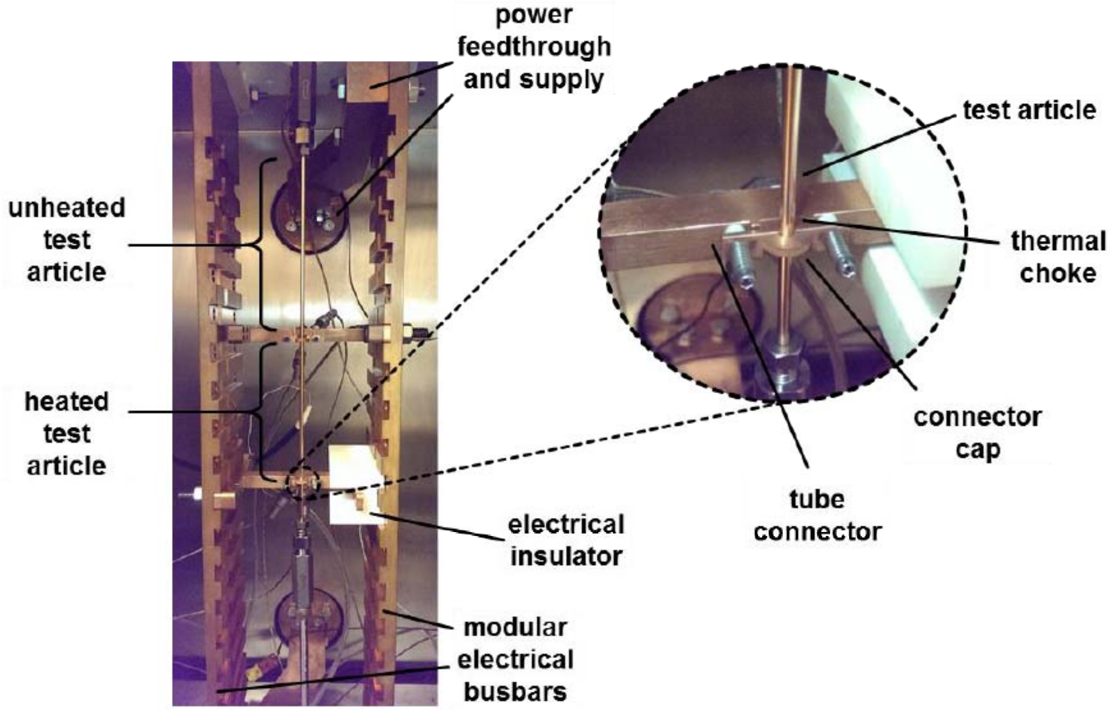


Fuel Set Compositional Variation





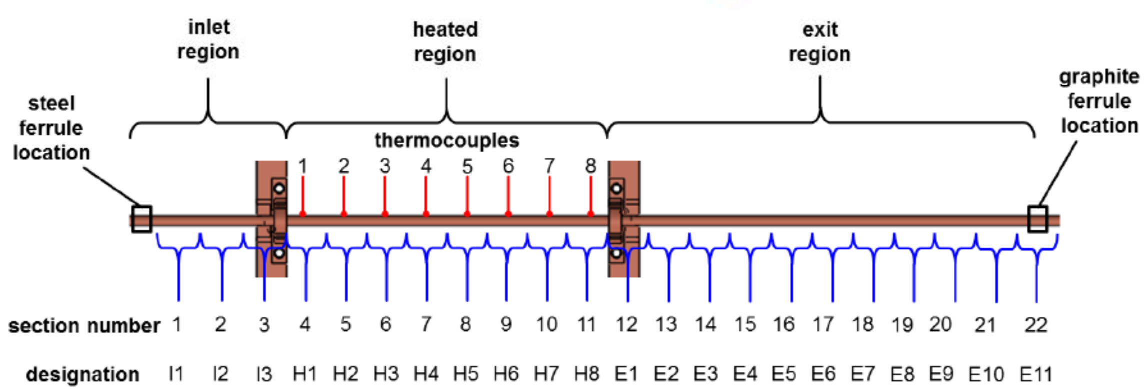
Compact Rapid Assessment of Fuel Thermal Integrity (CRAFTI)



Standard Test Conditions

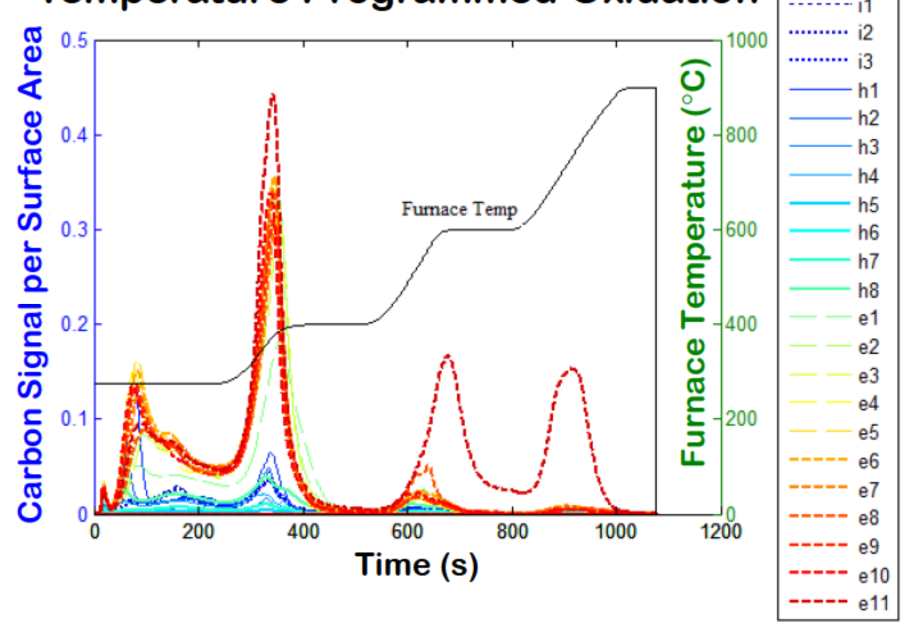
Parameter	Value	Units
Reynolds Number, Re	2000-20,000	-
Test article material	Cu (C10100)	-
Input power	4500	W
Wall temperature (dependent variable)	~1050±250 (560±120)	°F (°C)
Backpressure	1,000 (6.9)	psi (MPa)
Heated length	4 (10.2)	in. (cm)
Test duration	15	min.

Test Article Details & Naming



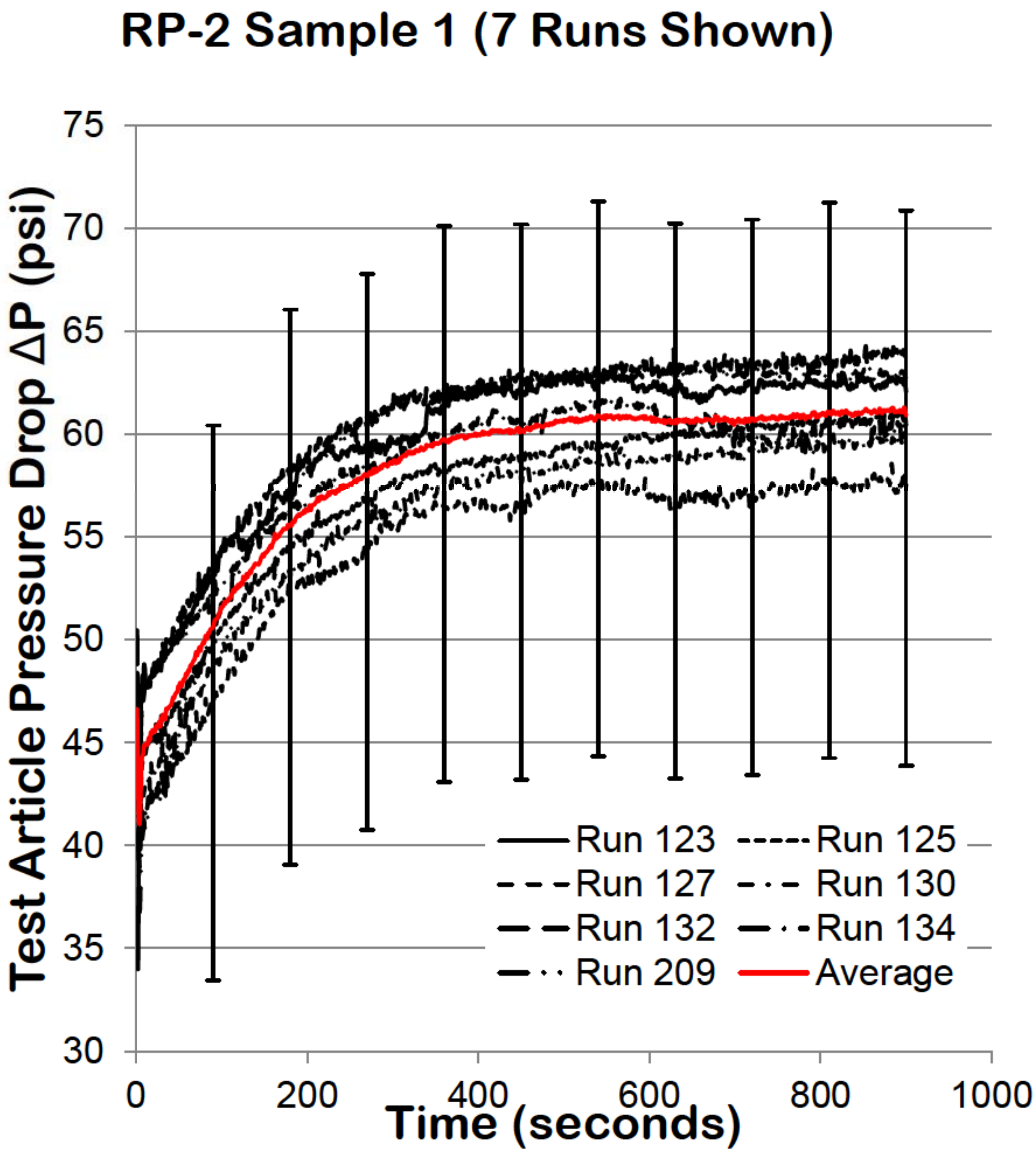
Test Article Analysis

Temperature Programmed Oxidation

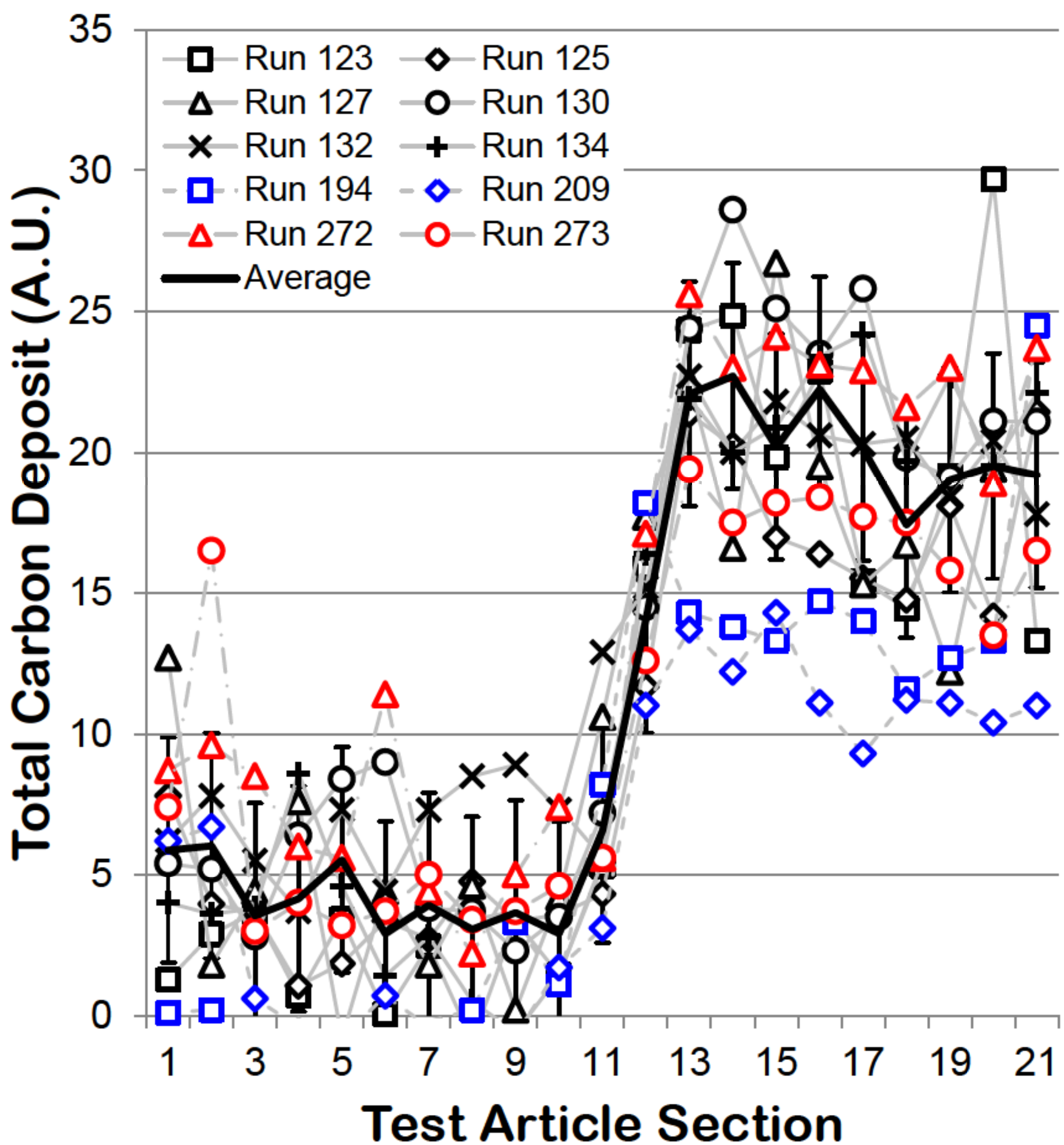


Repeatability: Pressure Drop Increase

- ***Ten runs were performed at standard test conditions using baseline fuel (RP-2 Sample 1)*** :
  - 6 runs – initially
  - 2 runs – 2/3 mo. later
  - 2 runs – 9/10 mo. later
  - Purge/flush/purge protocol between fuels; no disassembly
- Pressure drop *can be* indicative of deposit formation
  - Variation from other sources should be minimized
- Pressure drop variability from test to test was well within measurement uncertainty
  $\delta(\Delta P) \cong \delta(P_{\text{in}}) + \delta(P_{\text{out}})$



Repeatability: Deposit Formation



- For ten runs with baseline fuel, carbon deposit behavior is similar – and initially somewhat unexpected
- Near detection limits → some noise likely due to instrument response
- These results indicate “end-to-end” variation (fuel, experiment, test article handling, analysis, etc.)
- Will carbon deposit behavior vary with fuel composition?

CRAFTI Results Indicate Method Sensitivity for Thermally Stable Fuels

CRAFTI v1.1 Conditions/Results (15 min., $T_{o,bulk}$ ~ 650°F, T_{wc} ~ 800-1200°F)

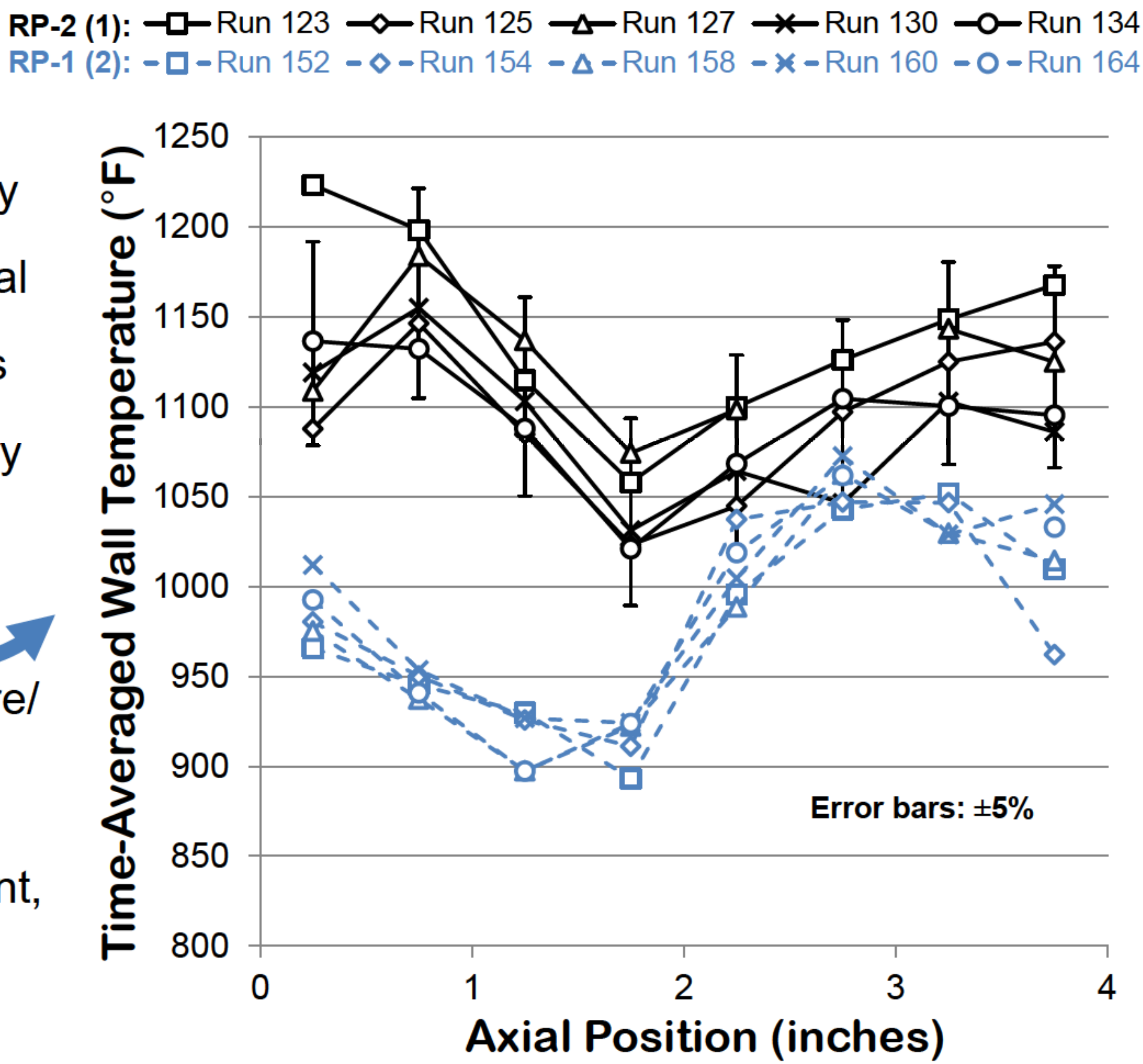
(Shaded fuels: Indistinguishable ΔP with JFTOT)

Fuel	Sample #	# of Runs	Average Wall Temperature °F (°C)	Pressure Drop ΔP, initial psi (kPa)	ΔP Increase during Test psi (kPa)
RP-2	1	10	1158 (626)	44 (306)	16 (113)
RP-2	4	4	1026 (552)	42 (288)	20 (136)
RP-2	7	2	1048 (564)	39 (269)	21 (142)
RP-1	3	7	1112 (600)	46 (320)	21 (146)
UL-RP-1	13	2	1115 (602)	33 (225)	22 (154)
RP-2	9	4	1110 (599)	31 (213)	23 (158)
RP-2	6	2	1145 (618)	47 (326)	23 (158)
RP-1	10	2	1057 (569)	31 (217)	26 (179)
RP-2	12	2	1144 (618)	29 (203)	30 (207)
RP-1	19	2	1074 (579)	26 (180)	30 (210)
RP-2	11	2	1085 (585)	30 (205)	33 (225)
RP-TS-5	14	2	1130 (610)	32 (222)	35 (242)
JP-900	16	2	1015 (546)	31 (217)	45 (313)
JP-7	15	2	950 (510)	30 (205)	50 (343)
RP-1	8	2	964 (518)	35 (241)	79 (545)
RP-1	5	2	985 (529)	41 (281)	82 (563)
RP-1	2	7	1027 (553)	45 (311)	91 (625)
RP-1	17	1	964 (518)	31 (217)	103 (713)
RP-1	18	2	1005 (541)	30 (210)	188 (1293)

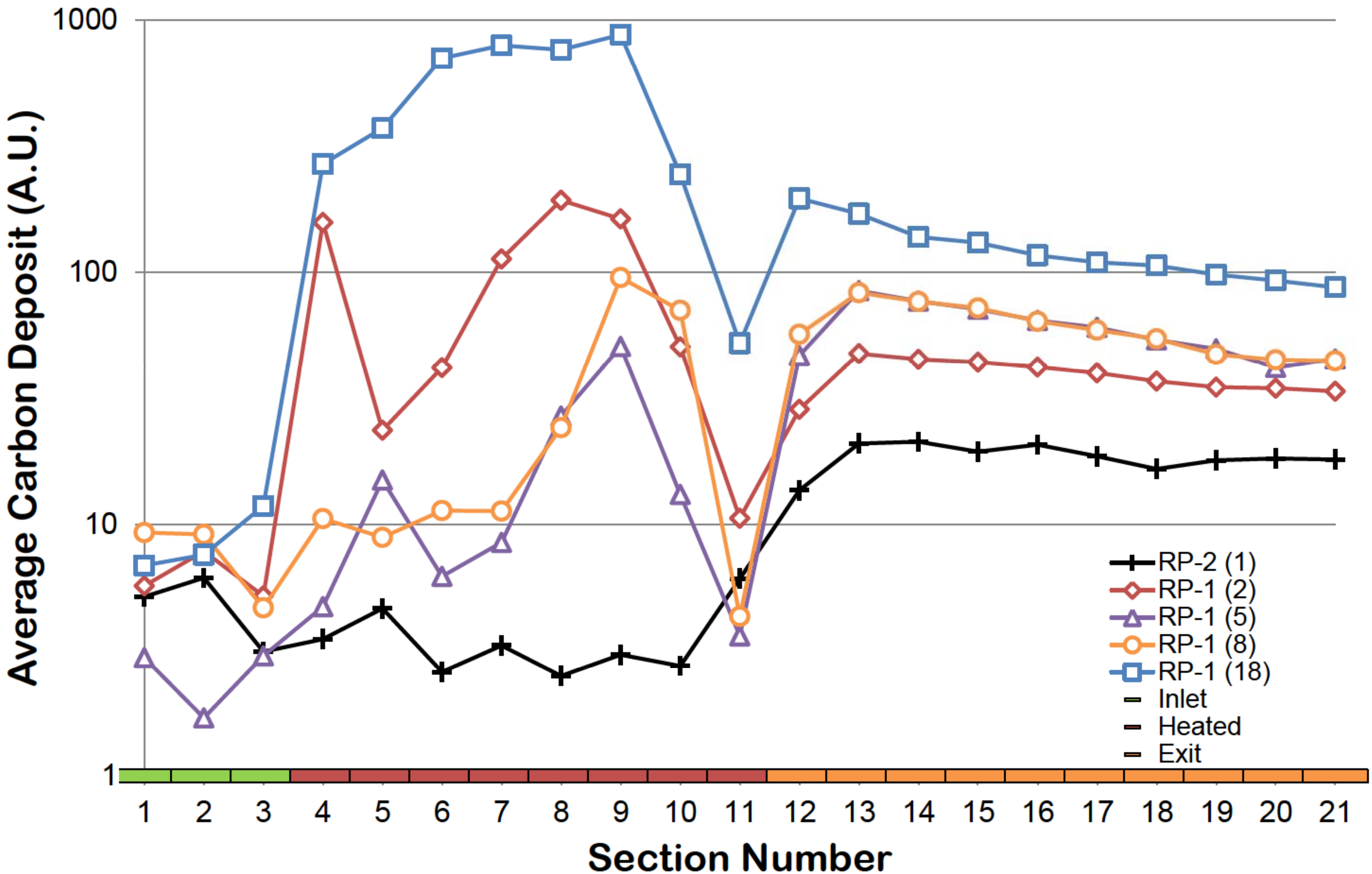
- Standard test conditions produce ***measureable performance differences***
- Pressure drop increase varies from 40-630% of initial value
- Most fuels meet current RP-1/RP-2 limits (MIL-DTL-25576E)
- JFTOT results indicated indistinguishable performance (ΔP increase after 5 hours) for these fuels

Wall Temperature Behavior (Heated Region Only)

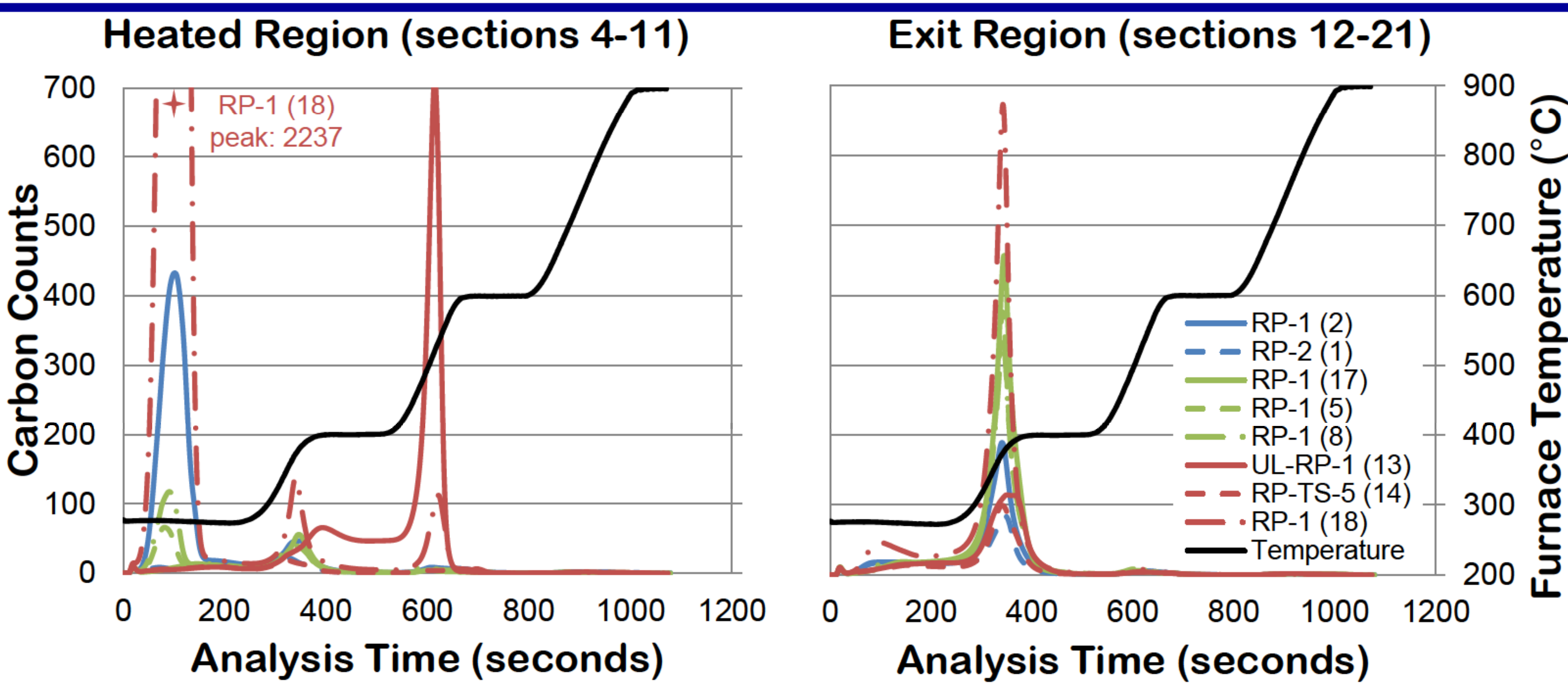
- Wall temperature *can be* indicative of fuel thermal integrity, but is complicated by other factors:
    - Electrical connection → local current flux density
    - Deposit formation → effects on local heat transfer
    - Transcritical flow → property gradients
- Repeatable characteristic profile for fuels of different thermal quality…
- Difficult to explain temperature/ time history variation
- Modeling & simulation underway to characterize fluid/solid thermal environment, flow behavior



Time-Integrated (Total) Carbon Sensitive to Fuel Composition

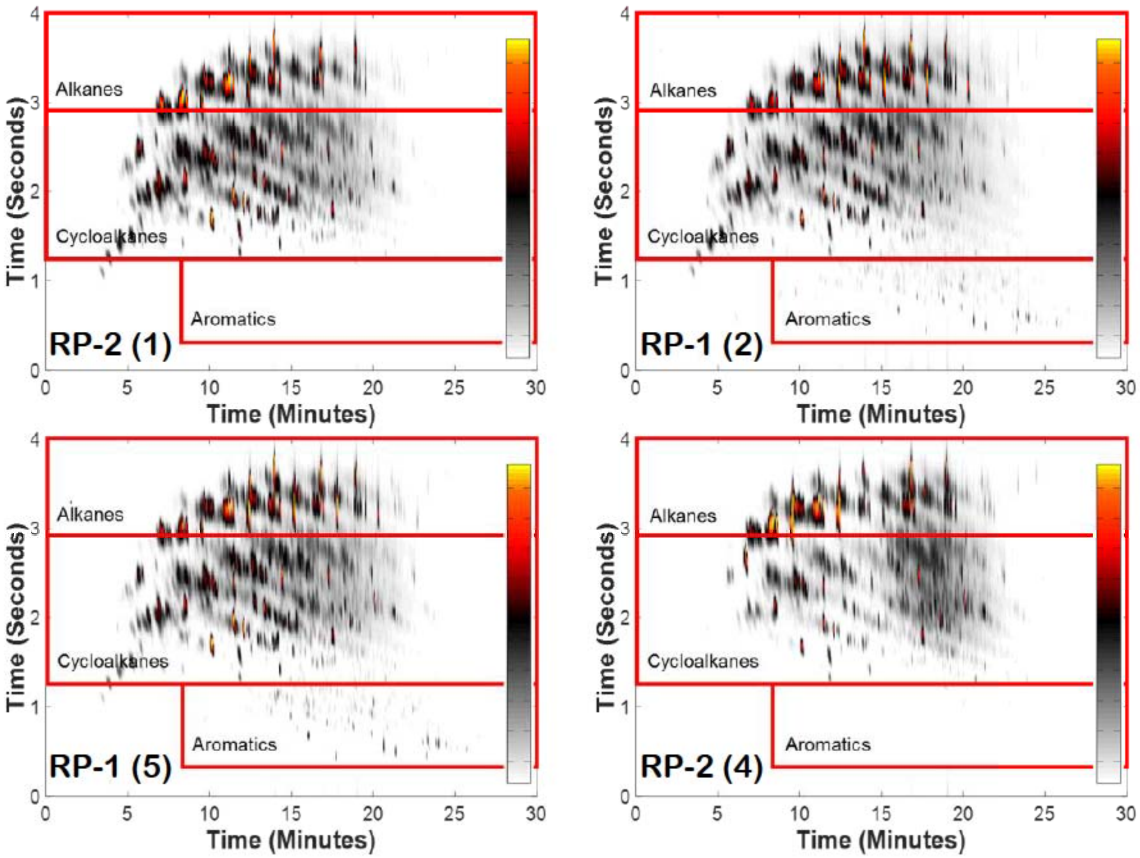


Differentiated Carbon Data Provides Additional Insight

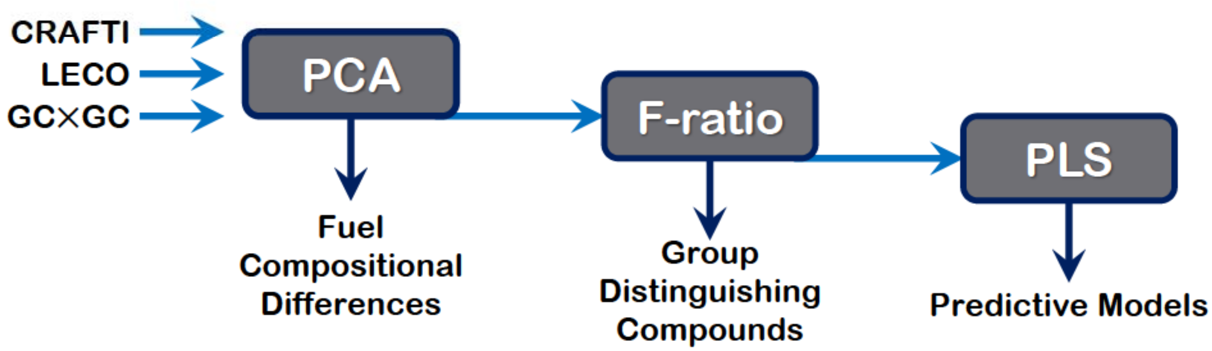


- Highest depositing fuels showed largest pressure drop increase
  - Exception: UL-RP-1 (13): significant deposit but small ΔP increase
- Heated region carbon deposits predominantly chemisorbed (0-200s)
- Amorphous carbon (200-450s) dominates exit region
- Only one fuel with strong filamentous carbon signal (450-800s): UL-RP-1 (13) in heated region
- Pressure drop increase correlated with amorphous deposit in exit region?

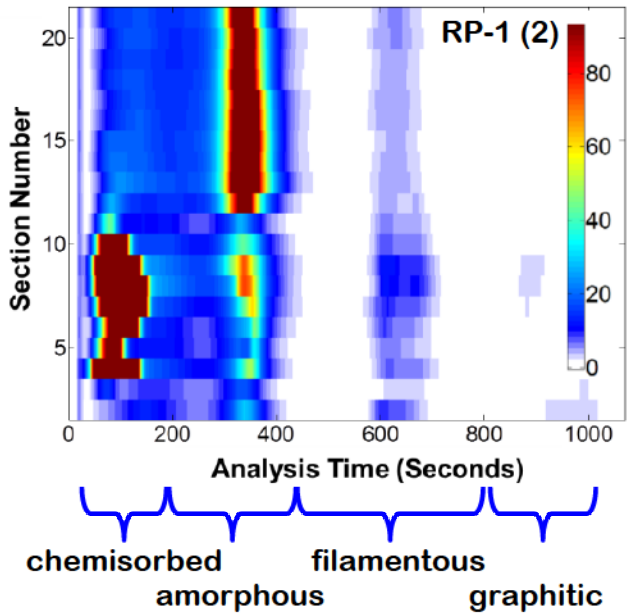
Chemometrics with CRAFTI, Carbon Deposit, & Comprehensive GC×GC-TOFMS Datasets



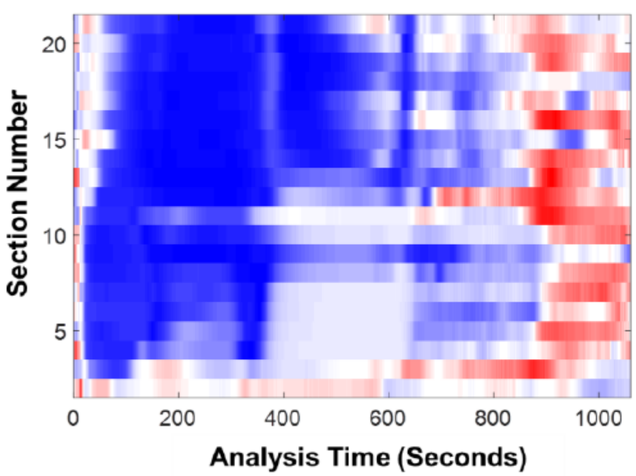
- Purpose of chemometrics: *Clarify role of fuel composition in cooling performance/quality*
  - Guide fuel formulation
  - Advise specification methods/limits
- Implementation:
  - Principal component analysis (PCA)
    - Assign categorical quality
    - Identify important compositional differences
  - Fisher ratio (F-ratio) analysis
    - Refine GC×GC dataset for optimized models
    - Identify distinguishing chemical compounds
  - Partial least squares (PLS) modeling
    - Develop predictive models that relate thermal integrity behavior to fuel composition



PCA Example: Correlate Carbon Deposit Types/Regions with Channel ΔP Increase

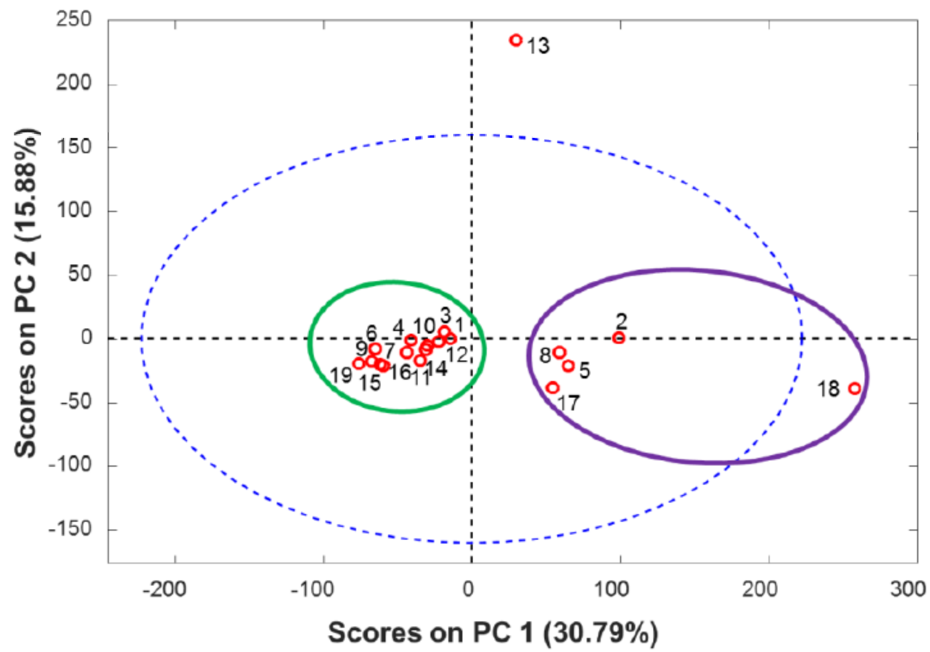


- Map of 3D TPO data
- Available for 19 referee fuels
- Multivariate data: excellent PCA candidate
- How can information be made useful?



- PCA PC1 Loadings Plot
- Associates positive (blue) & negative (red) contributions to PC1 with original data matrices
- Positive contributions to PC1 (blue) correlate with high pressure drop
- ΔP most sensitive to amorphous carbon (200-450s) in exit region (sections 12-21)

- PCA Scores Plot: PC groupings capture variance in measured data (ideally 100%)
- In this case, high ΔP fuels (purple) and low ΔP fuels (green) group together – primarily along PC1
- A relationship between carbon deposit and pressure drop is confirmed – but what does PC1 represent?

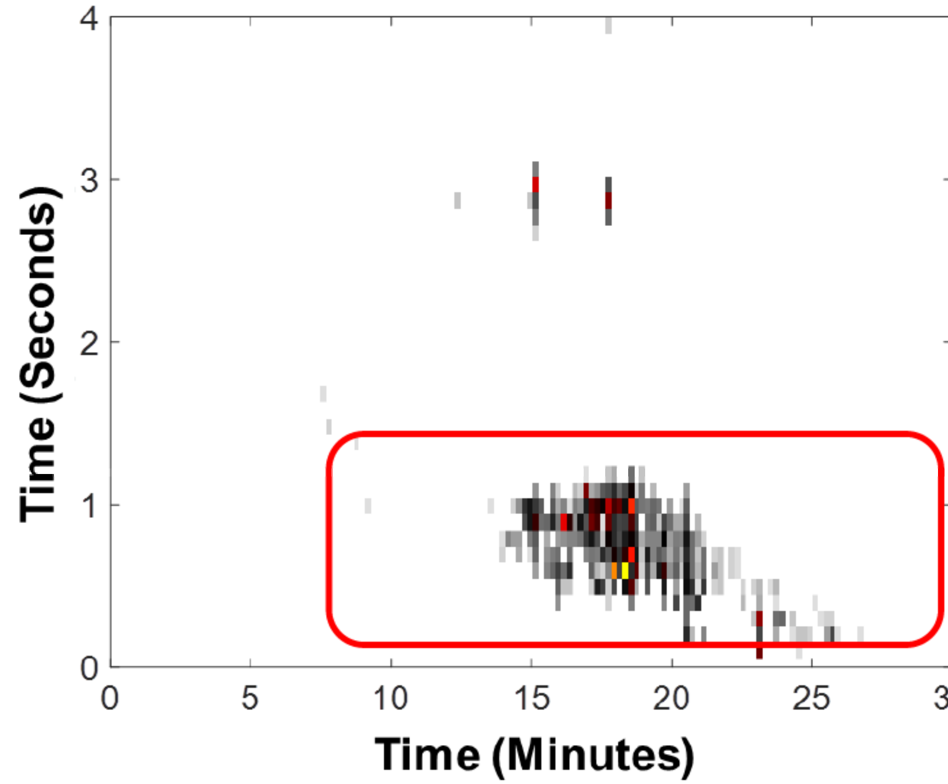


Similar analyses performed for test article pressure drop, wall temperature, GC×GC-TOFMS chromatographic variation

Fisher Ratio Analysis: Identify Compounds Responsible for Group Assignment

#	F-Ratio	t_r^1 (min.)	t_r^2 (sec)	Compound	Match Value	C-ratio
1	277.1	18.7	0.91	1,1,6-trimethyltetralin	908	13.0
2	254.1	18.3	0.97	5-ethyltetralin	846	15.9
3	233.0	18.7	1.01	(1,4-dimethylpent-2-enyl)benzene	769	16.9
4	231.4	18.8	0.96	1-methyltetralin	751	6.3
5	219.4	16.5	1.20	(1-ethylbutyl) benzene	790	14.5
6	214.0	15.6	1.31	5-methylnonane	840	1.7
7	201.3	18.1	1.31	1,3,5-trimethyl-2-propylbenzene	894	11.9
8	188.5	23.6	0.64	2,6-dimethyl naphthalene	935	68.3
9	188.2	18.2	3.31	2,6-dimethyl heptadecane	900	5.0
10	182.9	17.3	1.43	Adamantane	885	2.4
11	179.4	17.6	1.29	1-ethyl-2,4,5-trimethylbenzene	792	16.0
12	177.6	23.5	0.41	Biphenyl	926	34.8
13	175.9	18.5	1.31	6-propyltetralin	735	9.1
14	172.4	18.9	0.81	6-methyltetralin	955	16.4
15	171.4	19.1	0.91	2,3-dimethyltetralin	711	4.6
16	169.0	17.5	1.31	1,4-dimethyl-2-(2-methylpropyl)-benzene	825	13.3
17	167.9	18.8	1.13	1-heptenylbenzene	794	10.1
18	164.6	17.7	1.19	(5-methyl-1-hexenyl)benzene	764	13.8
19	162.7	18.8	1.33	(1-methylhexyl) benzene	818	18.4
20	161.9	15.4	1.25	p-cymene	814	6.9

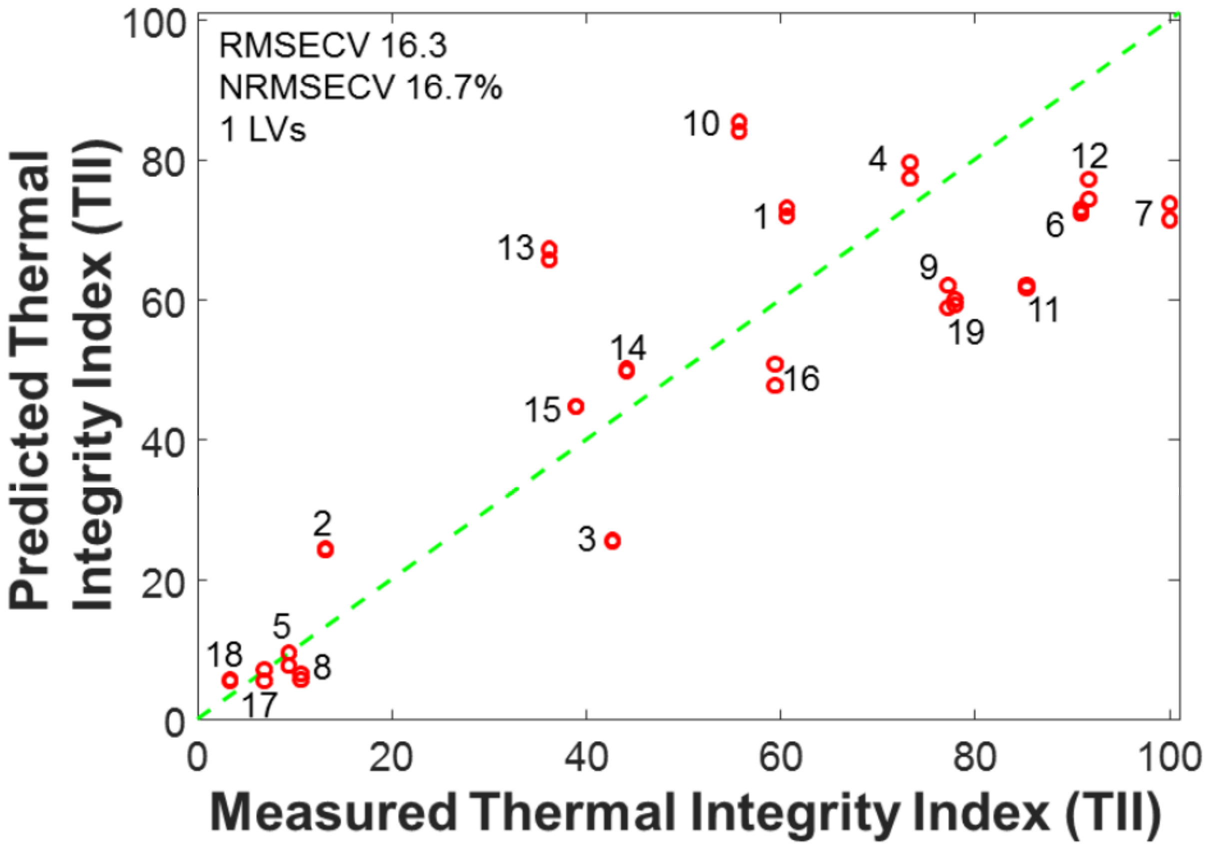
Top 300 F-Ratio Chromatographic Locations



- F-Ratio Analysis top hits are primarily aromatic…
- But their relative influence is quantified
- Hits represent class-distinguishing compounds, not necessarily direct influences on fuel thermal integrity
- Reduces superfluous chemical data in PLS model development

PLS Modeling: Predict Thermal Integrity using GC×GC-TOFMS Data

- Leave One Out Cross Validation (LOOCV):
  - *N* models generated, each with *N*-1 datasets
  - Datasets include CRAFTI, TPO, and GC×GC data
  - Each resulting model used to predict behavior for fuel *left out* during model generation
  - Statistical/graphical comparison of predicted vs. measured values
- Top 300 F-Ratio tiles used
- New parameter defined based on PCA, F-Ratio efforts: Thermal Integrity Index (TII):
  - $TII \propto \left(\Delta P_{\max} \times C_{A,\mathrm{exit}}\right)^{-1}$
- Good model agreement
  - Not inclusive of all compositional influences
  - Does not account for ΔP_{init}



Similar predictive models developed for test article pressure drop, wall temperature, carbon deposit

Summary

- A compositionally diverse set of rocket kerosene fuels was acquired and systematically evaluated
- A compact, rapid fuel thermal integrity assessment (CRAFTI apparatus) was developed and used to quantify fuel performance. Qualification criteria:
  - Operates at conditions *relevant* to intended application
  - Produces meaningful data quickly using small fuel quantity
  - Performance data collected with adequate repeatability
  - Discriminate between otherwise indistinguishable fuels
  - Results are *traceable* to existing experiments
  - Possesses characteristics of a *standard test method*
- Chemometric analyses applied to multiparametric datasets
  - Improvements in understanding of physicochemical influences and impacts of deposit formation were made
  - Predictive, composition-based models were developed – these models are *adaptable to additional datasets* and *expandable to diversified fuel sets*:
    - Pressure drop, wall temperature, carbon deposit, etc.

Thank You for Your Attention